

UNCLASSIFIED

DTIC FILE COPY

(4)

AD-A198 005

DOCUMENTATION PAGE

Form Approved
OMB No 0704 0188

1a REPORT SECURITY CLASSIFICATION Unclassified			1b RESTRICTIVE MARKINGS	
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited	
2b DECLASSIFICATION/DOWNGRADING SCHEDULE				
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 5			5 MONITORING ORGANIZATION REPORT NUMBER(S)	
6a NAME OF PERFORMING ORGANIZATION Naval Research Laboratory	6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c ADDRESS (City, State, and ZIP Code) 4555 Overlook Ave., SW Washington, DC 20375-5000		7b ADDRESS (City, State, and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, VA 22217-5000		
8a NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-87-WX-24204		
8c ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217-5000		10 SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO	PROJECT NO	TASK NO
		WORK UNIT ACCESSION NO		
11 TITLE (Include Security Classification) Unclassified Technical Report No. 5. Adsorption of Chlorine on Clean and on Oxygen Pre-Exposed Al(111).				
12 PERSONAL AUTHOR(S) V.M. Bermudez and A.S. Glass				
13a TYPE OF REPORT Technical	13b TIME COVERED FROM Oct. 86 TO Sept. 87	14 DATE OF REPORT (Year, Month, Day) 88/8/1	15 PAGE COUNT 19	
16 SUPPLEMENTARY NOTATION				
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
19 ABSTRACT (Continue on reverse if necessary and identify by block number)				
<p>The adsorption of Cl₂ on clean and on O₂ pre-exposed Al(111) has been studied using Auger and electron energy loss spectroscopies, low energy electron diffraction, temperature programmed desorption and work function measurement. Near room temperature chlorine forms a disordered layer in a two-step process consisting of adsorption at surface sites, dominating at low exposure, followed by population of subsurface sites at higher exposure. Surface adsorption is characterized by a sticking coefficient of about 0.1, an increase in work function of about 1 eV and a desorption peak at about 200°C. The subsurface phase exhibits a smaller sticking coefficient and work function change and no distinct desorption peak. Pre-adsorbed O blocks formation of subsurface species but not those formed in the initial adsorption step. Cl₂ does not displace pre-adsorbed O, but O₂ displaces some subsurface Cl. Chlorination is found to occur inhomogeneously rather than uniformly in a layer-by-layer mode.</p>				
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a NAME OF RESPONSIBLE INDIVIDUAL J.E. Butler			22b TELEPHONE (Include Area Code) (202) 767-1115	22c OFFICE SYMBOL 6174

OFFICE OF NAVAL RESEARCH

Contract N00014-87-WX-24204

R&T Code 413e009

Technical Report No. 5

Adsorption of Chlorine on Clean and on Oxygen
Pre-Exposed Al(111)

by

V.M. Bermudez and A.S. Glass

Prepared for Publication

in the

Journal of Vacuum Science and Technology

Naval Research Laboratory
Washington, D.C. 20375-5000

August 1, 1988

Reproduction in whole or in part is permitted for
any purpose of the United States Government

*This document has been approved for public release
and sale; its distribution is unlimited

* This statement should also appear in Item 10 of the Document Control Data-DD Form
1473. Copies of the form available from cognizant contract administrator.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

ADSORPTION OF CHLORINE ON CLEAN AND ON OXYGEN PRE-EXPOSED Al(111)

V.M. Bermudez and A.S. Glass*

Naval Research Laboratory

Washington, DC 20375-5000

PACS Nos. 81.60.-j, 79.20.-m

ABSTRACT

The adsorption of Cl₂ on clean and on O₂ pre-exposed Al(111) has been studied using Auger and electron energy loss spectroscopies, low energy electron diffraction, temperature programmed desorption and work function measurement. Near room temperature chlorine forms a disordered layer in a two-step process consisting of adsorption at surface sites, dominating at low exposure, followed by population of subsurface sites at higher exposure. Surface adsorption is characterized by a sticking coefficient of about 0.1, an increase in work function of about 1 eV and a desorption peak at about 200°C. The subsurface phase exhibits a smaller sticking coefficient and work function change and no distinct desorption peak. Pre-adsorbed O blocks formation of subsurface species but not those formed in the initial adsorption step. Cl₂ does not displace pre-adsorbed O, but O₂ displaces some subsurface Cl. Chlorination is found to occur inhomogeneously rather than uniformly in a layer-by-layer mode.

* NRL/ONT Postdoctoral Research Associate

INTRODUCTION

The oxidation of Al (by O₂ or H₂O) is one of the more thoroughly studied reactions in contemporary surface science¹. The full range of available techniques has been applied to the O₂/Al system, and a detailed mechanism for at least the initial stages of the oxidation process has been formulated^{2,3}. However, little work has been done on the reaction of Al with other oxidizers such as halogens. In particular, the reaction of Cl₂ with Al is important as a basis for "dry processing" in the fabrication of integrated circuit interconnections. Because of the reactivity of Al with O₂ and H₂O and the nearly unavoidable presence of such contaminants in realistic processing environments, it is also necessary to understand the effects of adsorbed O on the Al-Cl₂ reaction.

Early work for Cl₂ on polycrystalline Al⁴, using Auger electron spectroscopy (AES), measurement of the work function change ($\delta\Phi$) and ellipsometry, suggested adsorption in a molecular precursor state which then dissociates to give chemisorbed Cl. Most recent work⁵⁻¹² has been done in the context of plasma etching of Al in Cl-containing media. Etching of clean (i.e., oxide-free) Al by Cl₂ occurs spontaneously at room temperature and above^{6,8-11} and is not significantly enhanced by either gas-phase predissociation¹¹ of the Cl₂ or simultaneous ion bombardment^{6,8}. The room-temperature etch rate, roughly proportional to Cl₂ pressure in the 10⁻⁷ to 10⁻⁵ torr range, is about 1 Å/min at 10⁻⁷ torr⁸; the rate for HCl is much slower⁶. The desorbing species⁹ is mainly Al₂Cl₆ near 25°C and AlCl₃ at about 200°C. Chemisorption of Cl occurs^{9,10} prior to the onset of rapid etching, and under steady-state conditions a surface chlorinated layer remains. In one of the few investigations of this layer, Park et al.⁸ reported Al 2p photoemission data showing satellites at about 2 and 3 eV higher binding energy than the substrate peak, suggesting two distinct AlCl_x surface species.

The goal of the present work is an understanding of the adsorption of Cl_2 on $\text{Al}(111)$ and the effects of pre-adsorbed oxygen on the Al-Cl interaction. AES, temperature programmed desorption (TPD) and $\delta\Phi$ measurements were used as the principal experimental techniques. Low energy electron diffraction (LEED) and electron energy loss spectroscopy (ELS) results will also be reported.

EXPERIMENTAL DETAILS

Details concerning the apparatus and sample preparation have been given previously¹³ in connection with infrared spectroscopic studies of $\text{O}_2/\text{Al}(111)$. The sample used was the well-polished 2.5-cm diameter specimen¹³; after Ar^+ -ion bombardment and annealing the total impurity level (C, O and Cl) was < 0.005 monolayers, based on tabulated AES sensitivity factors¹⁴. All experiments (except TPD) were done at a sample temperature of $32\text{--}42^\circ\text{C}$. ELS data (0.5 eV resolution) were obtained with a $0.1\text{ }\mu\text{A}$, 50 eV primary beam ($\delta E = 0.25\text{ eV}$ modulation, $d[\text{EN}(E)]/dE$ mode). For AES a $0.5\text{ }\mu\text{A}$, 3 keV beam ($\delta E = 2\text{ eV}$) was used, and scans were done quickly (5 eV/sec, 0.1 sec time constant) to minimize electron dose. The beam from the coaxial electron gun was incident normal to the surface. The data were frequently checked for electron beam effects (stimulated desorption or adsorption of Cl ¹⁵, C or O¹⁶). Where observed, such effects will be noted. TPD was performed using a computer-interfaced quadrupole mass spectrometer (QMS), with channel multiplier, fitted with a quartz-glass enclosure¹⁷ around the ionizer (removed for residual gas analysis, RGA). The heating rate was not constant, varying from 0.8 to $2.4\text{ }^\circ\text{C/sec}$. $\delta\Phi$ data were obtained, to within $\pm 20\text{ meV}$, using the retarding potential method and a 40 eV, $0.5\text{ }\mu\text{A}$ beam from the Auger gun. The sample current, I , vs bias, V , was measured, and the shift of the peak in dI/dV vs V with Cl_2 exposure gave $\delta\Phi$ directly. The Cl coverage on (and, therefore, the work function change of) the hot tungsten gun filament is expected to be very low¹⁸.

The Cl₂ (>99.5% pure) was used without further purification. The Cu gasket assembly of the leak valve (Varian 951-5106) was electroplated with Au to retard corrosion. Exposures are given in Langmuirs (L), where 1 L = 10⁻⁶ torr-sec = 2.41x10¹⁴ Cl₂/cm², and were performed under computer control¹³ by dynamic backfilling to 1-3x10⁻⁷ torr (turbopump valved off and ion pump left open to the chamber). The Cl₂ was evacuated to ≤8x10⁻¹⁰ torr before turning on any electron beam. Pressure was measured with either a nude hot-filament ionization gauge or a cold-cathode gauge; readings in both cases were the N₂-calibration values. The Cl₂ sensitivity relative to that for N₂ is estimated¹⁹ to be 1.9.

RGA (based on uncorrected parent-ion relative intensities) showed small amounts of CH₄, CO and CO₂. CO and CO₂ (and, presumably, CH₄) are known²⁰ not to react at low pressure with Al at 25°C in the absence of electron irradiation, and no C accumulation was seen during these experiments. The small quantity of H₂ detected was shown to have no effect on adsorbed Cl, unlike the case²¹ for Cl on Pt(111) and (110); no loss in Cl Auger signal was observed when the sample was first exposed to 10 or 50 L of Cl₂ and then to 10 L H₂. H₂O and O₂ were found at a level of (H₂O+O₂)/Σ(Cl₂) ≈ 1.2% (where "Σ" indicates the sum of all isotopic species), and, following exposure of a clean Al surface to 80 L Cl₂, the resulting O atomic fraction was about 0.05. However, later experiments using higher purity Cl₂ (total H₂O and O₂ level ≤0.4%) showed the same degree of O contamination, suggesting that the source may, in part, be reaction of H₂O in the UHV background with adsorbed Cl. For O₂ pre-exposed surfaces the additional O accumulated during Cl₂ exposure was negligible.

The major contaminant²² was HCl (probably formed by reaction of Cl₂ with H-containing species on internal surfaces of the chamber). Initially (i.e., for the first of a series of exposures) Σ(HCl)/Σ(Cl₂) was about 50% and decreased quickly to about 15% with successive exposures. These are

upper limits since experiments with different pumping rates and ionizer emissions show that a large part of the HCl seen in RGA is produced in the QMS ionizer. To assess the effect of HCl, a clean surface was exposed to a 1:1 mixture of HCl and DCl (a supply of pure HCl was not available). Based on 15% as an upper limit to the HCl concentration, 80 L of Cl₂ would involve 12 L of HCl. Exposure to 12 L of the HCl/DCl mix gave a Cl Auger peak smaller than that for 2 L Cl₂, indicating that HCl is much less reactive with clean Al than is Cl₂, as previously reported⁶. HCl is somewhat more reactive with an O pre-exposed Al surface, as reported²³ for Pb(110). Following a 5 L O₂ exposure, 12 L of HCl/DCl gave a Cl peak equivalent to about 5 L Cl₂ on the clean surface.

RESULTS and DISCUSSION

(a) Auger

Fig. 1 summarizes the AES data. The results (for a clean Al surface) were independent of whether Cl₂ pressure was measured with a hot-filament or cold-cathode ionization gauge, indicating that excitation or dissociation of Cl₂ by the hot filament is not a major factor in adsorption. There was no significant difference in Cl uptake for a clean unannealed Ar⁺-ion bombarded sample, indicating that surface disorder is not an important factor. A decrease in the rate of change of the Cl and Al peak-to-peak heights (PPH's) occurs at about 10-15 and 20-30 L, respectively. The shape of the main Al L_{2,3}VV peak (68 eV) does not change appreciably with Cl₂ exposure. Hence, the coverage (θ) can be estimated, assuming a partial monolayer adsorbed on top of the substrate, using $I(\theta)/I(0) = 1 - \theta[1 - \exp(-d/\lambda \cos\phi)]$, where $I(0)$ is the clean-surface Al PPH and $\phi = 42^\circ$ the electron collection angle. For $d = 2.17 \text{ \AA}$ (sum of Al and Cl covalent radii) and $\lambda = 3.5 \text{ \AA}$ (as for clean Al²⁴), $\theta \sim 0.61$ monolayers is obtained at 20 L. In the present discussion a monolayer is defined as a continuous layer of close-packed Cl atoms. Using the Cl₂ ion gauge correction given above and a value of $9.82 \times 10^{14} \text{ Cl/cm}^2$ at

$\theta = 1$ (based on a Cl van der Waals diameter²¹ of 3.6 \AA), one estimates an initial Cl₂ sticking coefficient of $S \approx 0.12$, vs 0.01 as reported by Smith⁴ for Al films. The difference arises mainly from the fact that Smith⁴ (using ellipsometry) determined that $\theta = 1$ was achieved at about 200 L. Other S values, measured under etching conditions^{8,9,11}, may not be directly comparable with the initial S.

Pre-adsorbed O has a striking effect on Cl uptake. As discussed in refs. 1-3, 13 and works cited, the initial oxidation of Al proceeds in three (possibly overlapping) phases. The first, in order of increasing coverage, is the population of isolated surface and subsurface sites, followed by the clustering of sites to form rudimentary patches of oxide and, finally, the slow growth of an aluminum oxide film. The different stages can be distinguished by, for example, Auger PPH plots and changes in the Al L_{2,3}VV line-shape^{2,3,13}. Under the present conditions, the second (third) stage begins at about 5 (20) L of O₂. For the O₂ pre-exposed surface the initial Cl uptake (up to about 15 L) is unaffected, but further adsorption is very slow (in comparison to the clean surface) beyond 20 L. Several experiments were done for lower (10 or 20 L) O₂ pre-exposures. The results are consistent with those in Fig. 1; namely, the Cl uptake at lower exposures is unaffected, while that at higher values is slowed. However, because of the significant electron beam effect on the Cl layer (as shown by points labelled "A" in Fig. 1) and the accumulation of small amounts of O during exposure of the unoxidized surface to Cl₂, the most meaningful comparison is between samples with and without a large (50 L) O₂ pre-exposure.

The question of desorption of one species by the other has been considered. Fig. 1 shows that Cl₂ exposure does not produce a significant desorption of pre-adsorbed O. In addition, only a small (<10%) loss in Cl signal was observed when surfaces pre-exposed to 10 L of Cl₂ were subsequently exposed to 100 L of O₂. However, a similar O₂ exposure reduced by

about 20% the Cl AES signal for clean Al pre-exposed to 80 L Cl₂, suggesting that the Cl species formed at high coverage are more readily displaced by O₂ than are those present at low coverage. These results may be compared with those for other metals. For Ag(331)²⁵, O₂ pre-exposure does not greatly inhibit Cl uptake, but O₂ does displace previously adsorbed Cl. For Ag(110), chlorination is found^{26,27} to inhibit subsequent uptake of oxygen. Clean Pb(110) is found²³ to be much less reactive with HCl than with Cl₂ unless pre-exposed to O₂, in which case HCl reacts with surface oxide to form a chlorinated layer with desorption of H₂O. O₂ does not displace Cl from Pb(110) pre-exposed to Cl₂.

We have considered (and dismissed) one possible explanation for the decrease in the rate of Cl uptake above 20-30 L; namely, the onset of spontaneous etching⁸⁻¹⁰ (i.e., desorption of AlCl₃ or Al₂Cl₆). Two observations argue against this. First, previous work^{9,10} using a quartz crystal microbalance to measure etch rate indicates that near 25°C etching does not begin before Cl₂ exposures in excess of 10³ L. Second, with the sample in front of the QMS in a background of 2x10⁻⁷ torr Cl₂, no etch products were detected. For an etch rate⁸ of 1 Å/min the product flux rate would be about 1x10¹³/cm²-sec which would have been readily detectable.

(b) Work Function

Fig. 2 shows the $\delta\Phi$ results. In the first stage of adsorption $\delta\Phi$ increases to a maximum of +1.08 eV, suggesting that negatively charged species (e.g., Cl⁻ or Cl₂⁻) are formed "above" the surface. For a coverage of $\theta \approx 0.61$ and $\delta\Phi = +0.90$ at 20 L, one estimates $\mu \approx 0.40$ D (Debyes) for the surface-normal dipole. This value is comparable to those for Cl on the (111) surface of other face-centered cubic metals (0.14 D²¹ for Ni and 0.25 D²¹ or 0.56 D²⁸ for Pd), suggesting that the present estimate of Cl coverage on Al is reasonable. In the second stage, $\delta\Phi$ remains approximately constant, with some indication of a turn in the negative direction at higher exposure. The

nearly constant $\delta\Phi$, with a large increase in Cl coverage, indicates that either uncharged species are being formed or else ions are being distributed so as to produce only a small net contribution to the surface-normal dipole field (i.e., adsorption at surface and subsurface sites). Because of the high electronegativity of Cl, the latter explanation is considered more reasonable. Subsurface Cl adsorption may be accompanied by rearrangement of surface Al atoms to accomodate the large halogen species. Recently, concurrent surface and subsurface Cl adsorption has also been proposed for Cl₂ on Pb(110)²³ and on polycrystalline Mg²⁹ on the basis of angle-resolved core-level photoemission data. With pre-adsorbed O, a large positive $\delta\Phi$ is seen for a small Cl₂ exposure, followed by saturation of $\delta\Phi$ at a level well below that for the clean surface. The saturation value of $\delta\Phi$ was found to vary considerably from run to run for O₂ pre-exposed surfaces (unlike for clean Al), suggesting that $\delta\Phi$ is very sensitive to the distribution of Cl and O between surface and subsurface sites.

(c) Temperature Programmed Desorption

Fig. 3 shows the TPD data. AES indicated that heating to about 440°C, following a total of 80 L Cl₂, removed all near-surface Cl (through either desorption or subsurface diffusion) except for about 5% of the initial coverage. Cl was the only desorption product detected; Cl₂ and AlCl₃ were not observed, suggesting that Cl₂ adsorption is predominantly dissociative. Following Cl₂ exposure and recording of the TPD, another TPD scan was obtained as a "background". Subtraction from the original TPD then reduced the effect on the data of slow desorption of Cl from the sample holder, heater leads, etc. At sample temperatures above 300°C this "background" became significant, making TPD data difficult to obtain.

Following exposure of the clean surface to 10 L of Cl₂ a single broad peak was observed at about 200°C. The variation in temperature across the sample (observed using an infrared pyrometer) was much less than the width

of the TPD peak. "Calibration" vs the TPD of Ar implanted by 3 keV Ar⁺-ion bombardment (see Appendix) shows that the integrated intensity of the Cl TPD peak is accounted for by desorption of roughly 50% of the surface Cl; whereas, AES after TPD indicates a reduction of >90% in the Cl PPH. No increase in the integrated TPD peak intensity is observed for 50 L Cl₂; whereas, AES (Fig. 1) shows a large increase in the initial Cl coverage, and AES after TPD shows a reduction of about 75% in Cl PPH. This suggests that the 200°C peak is associated with Cl at surface sites, which saturate at lower exposures. For the subsurface Cl formed above 20 L no distinct TPD peak was detected. It is unknown at present whether the subsurface Cl desorbs over a very broad temperature range, desorbs in a peak above 350°C, or diffuses into the bulk. Subsurface diffusion, which has been noted previously^{4,9,10} for Cl on polycrystalline Al at room temperature, is considered the most likely explanation for the fact that not all the Cl at surface sites is accounted for by the 200°C TPD peak. Also unknown is the origin of the doublet structure in the Ar TPD and the significance of the fact that the Ar and Cl TPD peaks occur at nearly the same temperature.

(d) Model for Al Chlorination

The results are interpreted according to the following model. The Auger, $\delta\Phi$ and TPD results clearly indicate that Cl₂ adsorption is a two-phase process. At low exposure, Cl₂ is adsorbed rapidly at surface sites, giving $\delta\Phi > 0$ and a TPD peak at about 200°C. Above 20-30 L, Cl uptake occurs more slowly at subsurface sites (possibly accompanied by rearrangement of surface Al atoms), the occupation of which causes $\delta\Phi$ gradually to reach a positive maximum and then turn toward negative values. O₂ exposure sufficient to reach the "oxide" phase (≥ 20 L in this case) either depletes the subsurface sites or prevents their occupation by Cl, greatly slowing Cl uptake once the surface sites are filled. This mechanism then provides a basis for understanding how O inhibits the spontaneous etching of Al by Cl₂,

since formation of the precursor Cl-saturated surface layer^{9,10} is thus prevented. However, adsorbed O is also seen to have little or no effect on the initial chlorine uptake, suggesting that Cl and O occupy different surface sites. This is supported by the observation that O₂ does not significantly displace surface-site Cl, i.e., those species formed at low Cl₂ exposures.

On the basis of kinetic data (obtained at higher pressure, exposure and temperature than those used here), Smith⁴ proposed a somewhat similar two-step mechanism involving Cl₂ adsorption in a molecular precursor state followed by dissociation and reaction with the substrate. Since we cannot be certain whether the initial (surface) species is Cl⁻ or Cl₂⁻, the results and interpretation presented here are not inconsistent with those of Smith⁴ if we identify the surface species with Smith's molecular precursor and the subsurface species with the dissociated phase.

(e) Other Results - AES Lineshapes, ELS and LEED

Some attention was paid to the Al L_{2,3}VV lineshape (Fig. 4). For the O₂ pre-exposed surface, the "metal (Al⁰)" 68 eV peak, but not the 54 eV "oxide (Al⁺³)" peak³, is strongly attenuated by Cl₂ exposure, indicating that Cl preferentially occupies Al sites not multiply coordinated to O.

ELS data for clean Al were in accord with previous results³⁰. Cl₂ exposure caused a gradual decrease in intensity of the volume and surface plasmons, with nearly complete disappearance of the latter by 80 L. Cl-induced structure was seen at loss energies of $\delta E = 6.5$ and 19.5 eV, the latter being very weak and tentatively assigned to the Cl 3s \rightarrow 4p transition. Other, weaker losses^{30,31}, possibly related to the small level of O contamination incurred during Cl₂ exposure, were found at $\delta E = 3.5$, 7.5 and ~ 12 eV. The data do not agree well with the ELS³² of gas-phase Cl₂, as might be expected for a high concentration of physisorbed Cl₂ weakly interacting with Al. Vibrational ELS would be necessary for investigating the presence of Cl₂ or Cl₂⁻ (the latter having a Cl-Cl stretching mode³³ at $265 \text{ cm}^{-1} = 32.8$

meV).

Cl₂ exposure caused a gradual degradation of the (111)-(1x1) clean-surface LEED pattern (observed at 40-80 eV primary beam energies) with nearly complete disappearance by 80 L. However, after 40 L of Cl₂, for which the estimated average coverage (Fig. 1) is in excess of 1 monolayer, the LEED pattern is still clearly visible (and the Al surface plasmon is still present in ELS). These observations suggest chlorination in three-dimensional patches (rather than in a uniform film) and are consistent with the onset of subsurface Cl⁻ adsorption as deduced from the $\delta\Phi$ data. Annealing after a 40 or 80 L exposure caused a partial return of the pattern as the Cl coverage decreased; there was no indication of any ordered overlayer.

ACKNOWLEDGEMENT

This work was supported by the Office of Naval Research.

APPENDIX

The Cl TPD was "calibrated" using Ar TPD observed under the same conditions. The implanted Ar and adsorbed Cl AES intensities are given by $I_x = f_x N_x S_x$ ($x \equiv \text{Ar, Cl}$) where S_x is the Auger sensitivity factor¹⁴, N_x the number of implanted Ar/cm² or adsorbed Cl/cm² and f_x the fraction of atoms detected in AES. As discussed in the text, the adsorbed Cl produced by a 10 L Cl₂ exposure is believed to occupy predominantly surface sites, giving $f_{\text{Cl}} \approx 1$. f_{Ar} is estimated using

$$f_{\text{Ar}} = \int_0^{\infty} n(z) \exp(-z/\lambda \cos \phi) dz / \int_0^{\infty} n(z) dz$$

where $n(z)$ is the implanted-Ar distribution as a function of depth, z . Various functional forms for $n(z)$, e.g., symmetric Gaussian, joined half-Gaussian and Edgeworth functions, have been discussed by Gibbons et al.³⁴ The parameters needed to evaluate $n(z)$ for implantation of 3 keV Ar⁺ ions in Al have been calculated by Burenkov et al.³⁵ from which we obtain f_{Ar} in the range of 0.0067 to 0.010, depending on the expression used for $n(z)$. The ionizer of the gun used in these studies operates at a 200 eV electron ener-

gy, for which about 10% of the argon ions are Ar^{+2} (estimated using the energy dependence of the first- and second-ionization cross-sections³⁶); this has been neglected in computing f_{Ar} . The possible channeling of some of the ions along the [111] axis has also been neglected since the Ar^+ TPD data were obtained for samples already disordered by previous Ar^+ bombardment, and Ar "desorption" occurs well below the Al annealing temperature. The Auger PPH ratio $I_{\text{Cl}}/I_{\text{Ar}}$ then gives $N_{\text{Cl}}/N_{\text{Ar}} \approx 0.09$, i.e., for 10 L Cl_2 the number of adsorbed Cl/cm² is about 0.09 times the number of Ar^+ /cm² implanted at 3 keV. Comparison of the integrated intensities of the Cl and Ar TPD peaks (assuming equal QMS detection efficiency for Cl and Ar) then allows an estimate of the fraction of adsorbed Cl contributing to the Cl TPD peak.

REFERENCES

1. I.P. Batra and L. Kleinman, J. Electron Spectrosc. Relat. Phenom. 33, 175 (1984)
2. J.E. Crowell, J.G. Chen and J.T. Yates Jr., Surf. Sci. 165, 37 (1986)
3. J.G. Chen, J.E. Crowell and J.T. Yates Jr., Phys. Rev. B 33, 1436 (1986)
4. T. Smith, Surf. Sci. 32, 527 (1972)
5. D.W. Hess, Plasma Chem. Plasma Process. 2, 141 (1982)
6. D.L. Smith and P.G. Saviano, J. Vac. Sci. Technol. 21, 768 (1982)
7. D.L. Smith and R.H. Bruce, J. Electrochem. Soc. 129, 2045 (1982)
8. S. Park, L.C. Rathbun and T.N. Rhodin, J. Vac. Sci. Technol. A 3, 791 (1985)
9. H.F. Winters, J. Vac. Sci. Technol. B 3, 9 (1985)
10. W. Sesselmann and T.J. Chuang, J. Vac. Sci. Technol. B 3, 1507 (1985)
11. D.A. Danner and D.W. Hess, J. Appl. Phys. 59, 940 (1986)
12. R.J.A.A. Janssen, A.W. Kolfschoten and G.N.A. van Veen, Appl. Phys. Letts. 52, 98 (1988)
13. V.M. Bermudez, R.L. Rubinovitz and J.E. Butler, J. Vac. Sci. Technol. A

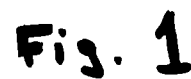
- 6, 717 (1988)
14. L.E. Davis, N.C. MacDonald, P.W. Palmberg, G.E. Riach and R.E. Weber, "Handbook of Auger Electron Spectroscopy" 2nd Ed. (Perkin-Elmer Corp., Eden Prairie (Minn.), 1978)
 15. S. Bouquet, J. Bergner, J. LeHéricky and J.P. Langeron, J. Electron Spectrosc. Relat. Phenom. 26, 247 (1982)
 16. S.A. Flödstrom and C.W.B. Martinsson, Applic. Surf. Sci. 10, 115 (1982); E.H. Adem, D.L. Seymour and E.B. Pattinson, Surf. Sci. 141, 1 (1984)
 17. P. Feulner and D. Menzel, J. Vac. Sci. Technol. 17, 662 (1980)
 18. H.M. Kramer and E. Bauer, Surf. Sci. 107, 1 (1981)
 19. T.A. Flaim and P.D. Ownby, J. Vac. Sci. Technol. 8, 661 (1971)
 20. C.B. Bargeron and B.H. Nall, Surf. Sci. 119, L319 (1982); A.F. Carley, D.E. Gallagher and M.W. Roberts, Surf. Sci. 183, L263 (1987)
 21. W. Erley, Surf. Sci. 94, 281 (1980); Surf. Sci. 114, 47 (1982)
 22. Yung-Yi Tu and J.M. Blakely, J. Vac. Sci. Technol. 15, 563 (1978)
 23. P.G. Blake, A.F. Carley, V. DiCastro and M.W. Roberts, J. Chem. Soc. Faraday I 82, 723 (1986)
 24. S. Tanuma, C.J. Powell and D.R. Penn, Surf. Sci. 192, L849 (1987)
 25. R.A. Marbrow and R.M. Lambert, Surf. Sci. 71, 107 (1978)
 26. C.T. Au, S. Singh-Boparai, M.W. Roberts and R.W. Joyner, J. Chem. Soc. Faraday Trans. I 79, 1779 (1983)
 27. C.T. Campbell and M.T. Paffett, Applic. Surf. Sci. 19, 28 (1984)
 28. W.T. Tysoe and R.M. Lambert, Surf. Sci. 199, 1 (1988)
 29. C.T. Au and M.W. Roberts, Surf. Sci. 149, L18 (1985)
 30. F. Pellerin, C. LeGressus and D. Massignon, Surf. Sci. 103, 510 (1981); B.H. Nall, A.N. Jette and C.B. Bargeron, Surf. Sci. 110, L606 (1981)
 31. A. Hoffman, T. Maniv and M. Folman, Surf. Sci. 193, 513 (1988)
 32. R.J. Stubbs, T.A. York and J. Comer, J. Phys. B 18, 3229 (1985)
 33. M. Hass and D.L. Griscom, J. Chem. Phys. 51, 5185 (1969)

34. J.F. Gibbons, W.S. Johnson and S.W. Mylroie, "Projected Range Statistics - Semiconductors and Related Materials" (Dowden, Hutchinson and Ross; Stroudsburg (PA); 1975). The discussion of the joined half-gaussian distribution in Section 4.3 of this reference contains several typographical errors. The correct expressions are given in J.F. Gibbons and S. Mylroie, Appl. Phys. Letts. 22, 568 (1973)
35. A.F. Burenkov, F.F. Komarov, M.A. Kumakhov and M.M. Temkin, "Tables of Ion Implantation Spatial Distributions" - Engl. Transl. by S.J. Amoretty (Gordon and Breach, New York, 1986)
36. H.S.W. Massey and E.H.S. Burhop, "Electronic and Ionic Impact Phenomena" (Clarendon, Oxford, 1952)

FIGURE CAPTIONS

1. AES first-derivative peak-to-peak heights (PPH's), vs Cl₂ exposure, for Al with 0 and 50 L O₂ pre-exposures. All plots are on the same scale. Points labelled "A" show the results for a new spot on the sample (not previously irradiated by the AES primary beam) following the last Cl₂ exposure. The clean-surface data show the small O uptake occurring during large Cl₂ exposures. The dashed line indicates the O detection limit under the rapid-scan conditions used to obtain these data. The relative sensitivities for the main Auger peaks are approximately Cl LMM (181 eV) : O KLL (510 eV) : Al LVV (68 eV) = 4 : 2 : 1 (ref. 14). All exposures are based on ion gauge readings uncorrected for the Cl₂/N₂ relative sensitivity.
2. $\delta\Phi$ vs Cl₂ exposure for Al with 0 and 51 L O₂ pre-exposures. The results for two separate clean-surface experiments are shown. For 51 L O₂, the negative $\delta\Phi$ at 0 L Cl₂ represents the effect of O₂ on the clean surface. Also shown are the results for O₂ exposure following exposure of the clean surface to 90 L Cl₂. The uncertainty of ± 0.02 eV (same for each point) is indicated.

3. Temperature programmed desorption data (35 amu Cl) for clean and ordered Al(111) exposed to 10 Cl₂. Also shown is the 40 amu Ar desorption following 10 min of Ar⁺-ion bombardment at 3 keV and about 6 μA/cm² at normal incidence.
4. Al L_{2,3}VV lineshape (and other Auger features) for clean Al, after 50 L O₂ and after a subsequent 35 L Cl₂ exposure. The data show the attenuation of the Al⁰ peak relative to the Al⁺³ peak by Cl₂ and, incidentally, the small Cl uptake occurring during a large O₂ exposure.



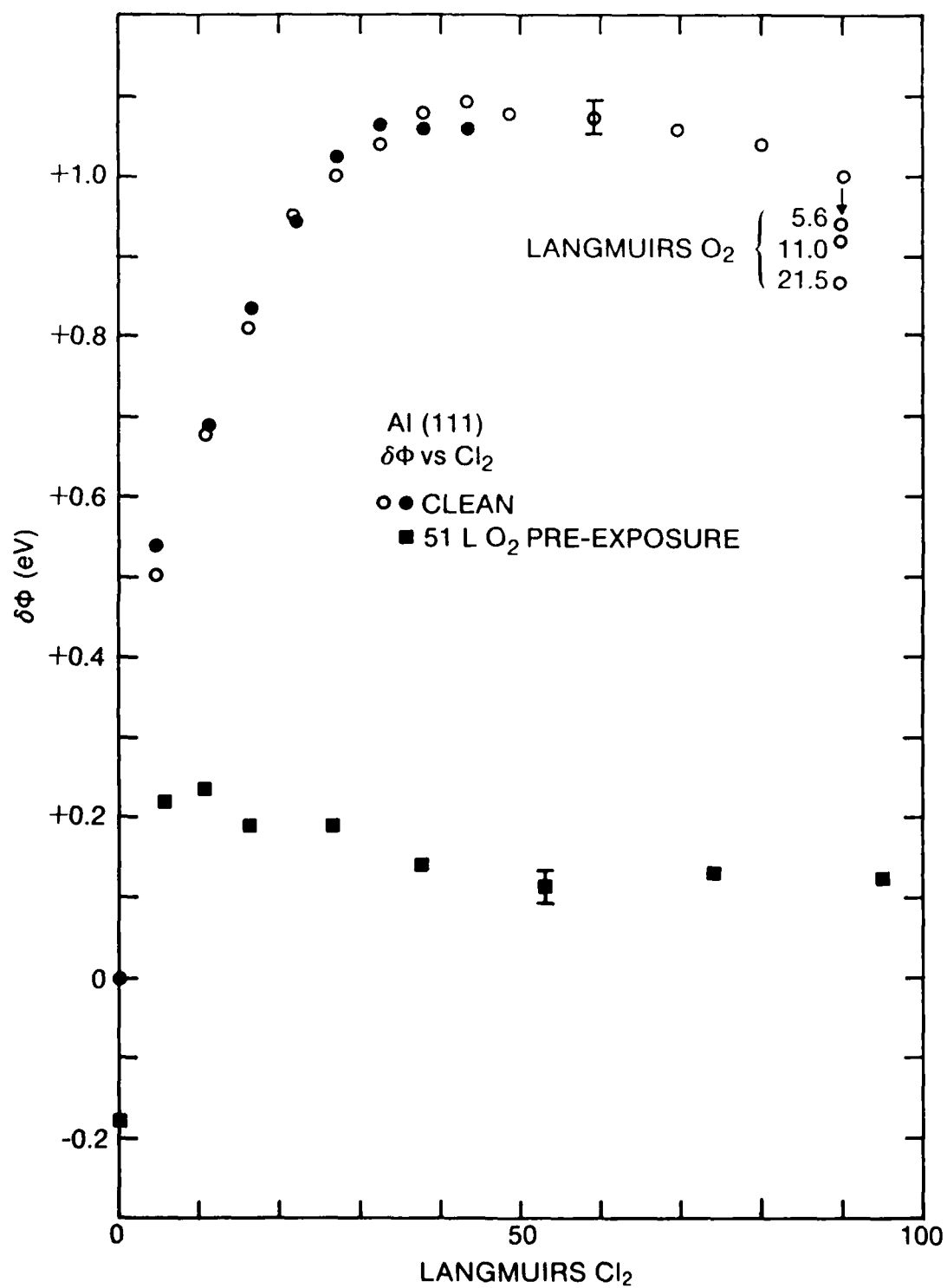


Fig. 2

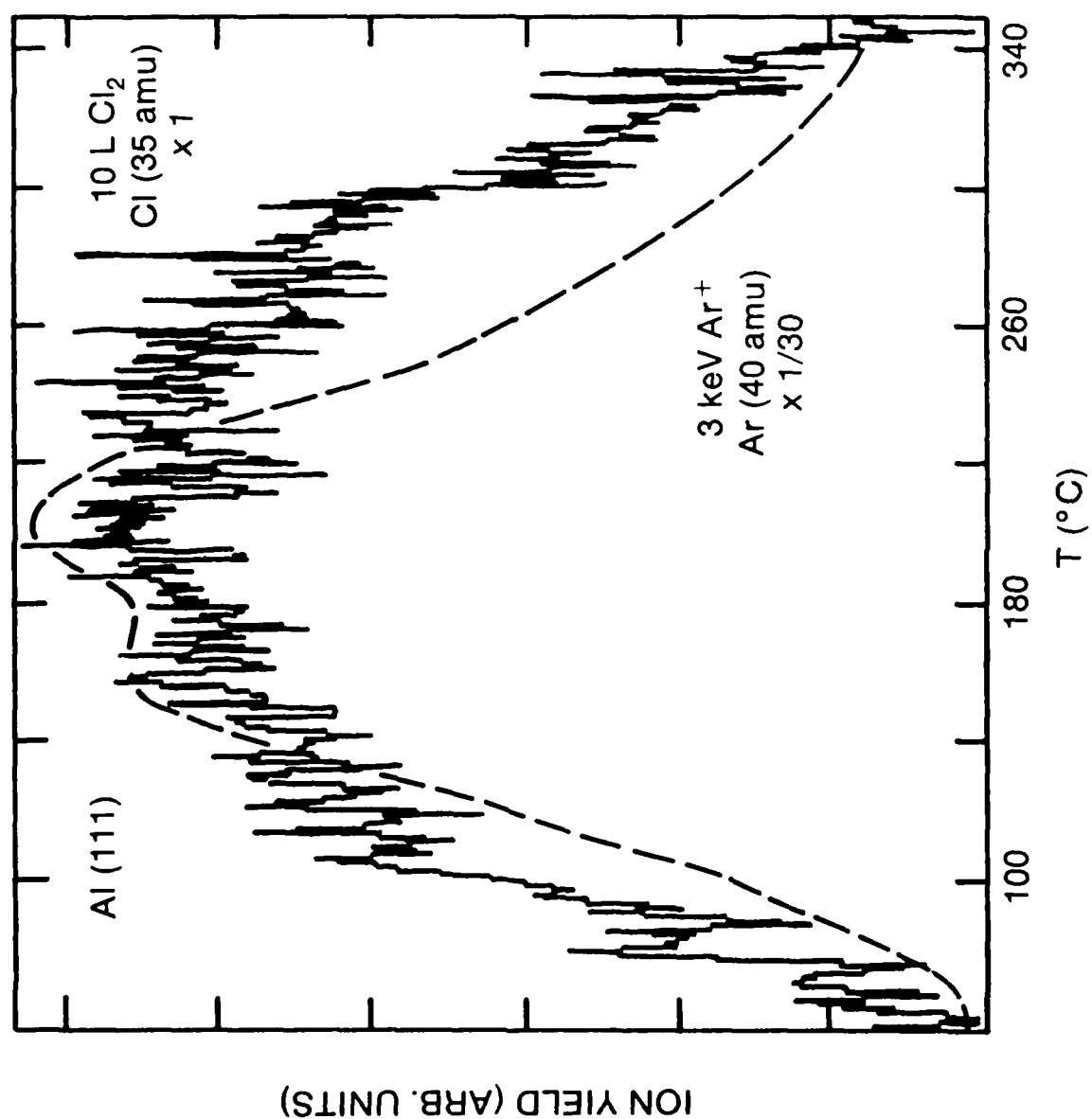


Fig. 3

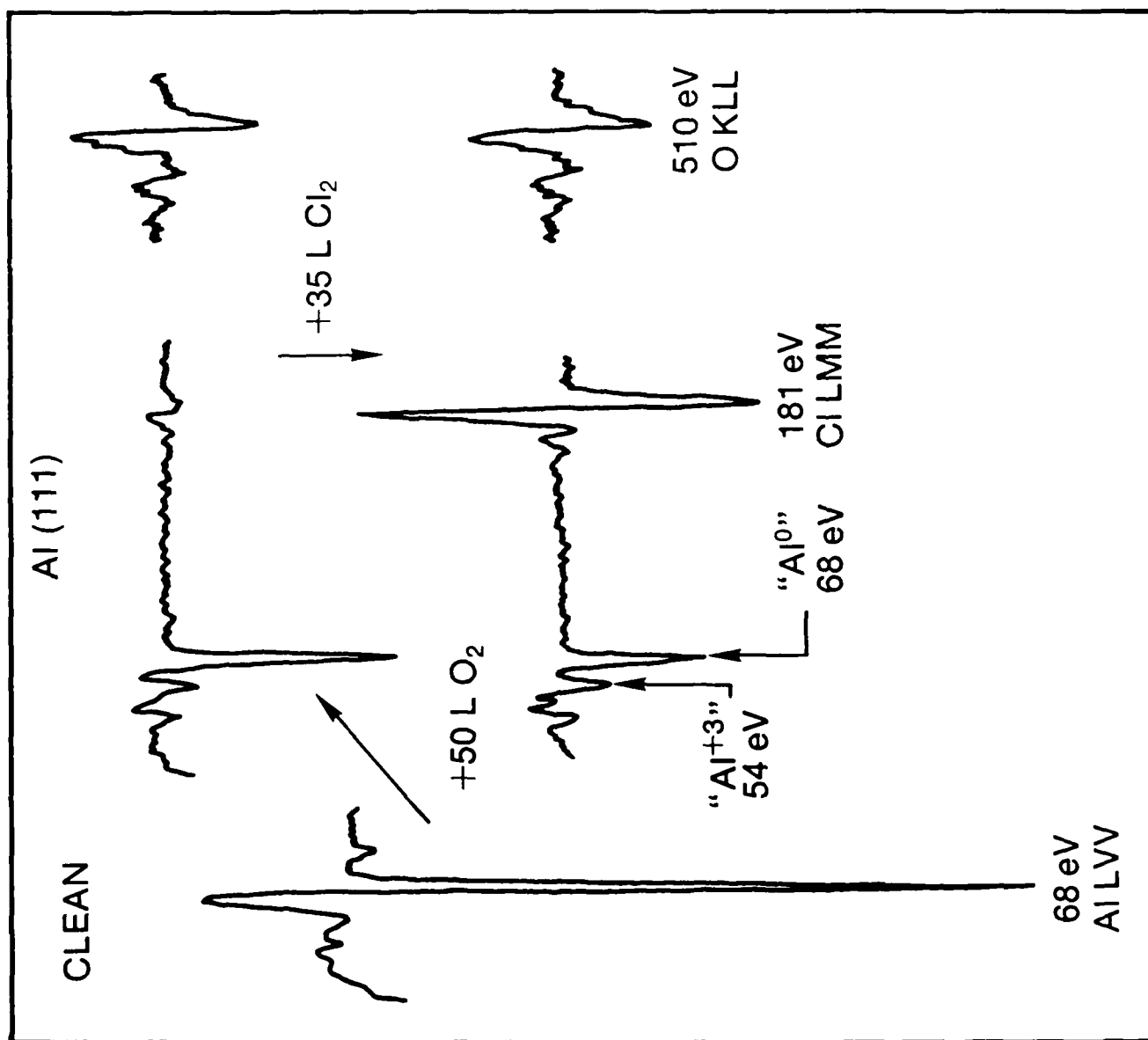


Fig. 4